



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : G01N 1/10, 1/20		A1	(11) International Publication Number: WO 99/00656 (43) International Publication Date: 7 January 1999 (07.01.99)
<p>(21) International Application Number: PCT/FI98/00519</p> <p>(22) International Filing Date: 16 June 1998 (16.06.98)</p> <p>(30) Priority Data: 972574 17 June 1997 (17.06.97) FI</p> <p>(71) Applicant (<i>for all designated States except US</i>): NESTE OY [FI/FI]; Keilaniemi, FIN-02150 Espoo (FI).</p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (<i>for US only</i>): TOLVANEN, Ilkka [FI/FI]; Saksala 103, FIN-06100 Porvoo (FI). WALDVO-GEL, Jürg [FI/FI]; Päiväläispolku 12 C, FIN-06450 Porvoo (FI). PIVLIO, Olli [FI/FI]; Gumbostrand, FIN-01150 Söderkulla (FI).</p> <p>(74) Agent: FORSSÉN & SALOMAA OY; Yrjönkatu 30, FIN-00100 Helsinki (FI).</p>		<p>(81) Designated States: AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published With international search report. In English translation (filed in Finnish).</p>	
<p>(54) Title: AUTOMATIC SAMPLING AND TREATMENT SYSTEM</p> <p>(57) Abstract</p> <p>The present invention relates to an automatic sampling and treatment system (10) comprising a sampling loop (15) connected on-line to a process (11) to receive a sample stream from a stream (A) being processed in the process (11). The sampling loop (15) is further connected to an analyser to convey the sample stream from the sampling loop (15) to the analyser. The sampling loop (15) is connected to the process (11) with a first conduit (14), and with a second conduit (16). The sampling loop (15) is connected to the analyser with a third conduit (18), and to a feeding system of an additive with a fourth conduit (19). A first actuator (12) is adapted to open and close a valve (13a) in the first conduit (14), and a valve (13b) in the second conduit (16). A second actuator (21) is adapted to open and close a valve (2a) in the third conduit (18), and a valve (22b) in the fourth conduit (19).</p>			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Larvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

Automatic sampling and treatment system

5

The present invention relates to an automatic sampling and treatment system comprising a sampling loop connected on-line to a process to receive a sample stream from a stream being processed in the process, and further, connected to an analyser to convey the sample stream from the sampling loop to the analyser.

10

Continuously operating analysers are used in the chemical industry for quality control to determine concentrations or other important quality criteria from the process streams desired. One of the most important features of these on-line analysers influencing the performance thereof is a sampling system that functions 15 properly.

In the petroleum refining, dark and heavy, high boiling crude oil fractions and mixtures thereof are formed, and thereafter, used as starting materials to produce bitumen and heavy fuel oil. The poor solubility or the precipitation of asphaltenes 20 contained in these refined oil products impedes the application and storage thereof. The tendency of the asphaltenes to precipitate determines the stability, or the storability of these oil products, this tendency depending on the process, and the starting materials used in the production. Particularly the thermal cracking used at 25 present influences the tendency of the asphaltenes to precipitate. In the thermal cracking unit, the crude oil refining process is controlled in such a way that the heavy fuel oil obtained from the bottom of the unit were stable.

Traditionally, the stability of oil products is determined from samples taken with the so-called flocculation method, among others (for instance, the Shell method; 30 Flocculation ratio of bitumen and fuel oil). The method is based on the paper chromatography, and the visual evaluation of the chromatograms. With this method it takes 0,5-6 hours to obtain the results.

Automatic on-line analysers have also been developed, the function thereof being for instance the monitoring of the asphaltene content of the oil product, either directly from the production process, or by analysing the samples in a laboratory.

- 5 In case of an automatic on-line analyser, a process analyser controlled by a computer automatically takes a sample from the product stream desired, produces a parameter characterising the stability, and sends it to the control unit of the process at predetermined intervals, for instance every 10 minutes.
- 10 The object of the present invention is to improve the systems known at present.

The automatic sampling and treatment system of the invention is characterized in that the sampling loop is connected on-line to the process with a first conduit, and with a second conduit, the sampling loop is connected to the analyser with a third conduit, and to a feeding system of an additive with a fourth conduit, and that a first actuator is adapted to open and close a valve in the first conduit, and a valve in the second conduit.

In a preferable embodiment of the present invention a second actuator is adapted to open and close a valve in a third conduit, and a valve in a fourth conduit. The valve actuated by the second actuator is not necessarily needed in the third conduit, but can be replaced with a return valve. The second actuator is not necessary, since it may be replaced with a pump, if desired, allowing also the valves in the third and fourth conduits to be omitted, if desired.

25 The functioning of the sampling and treatment system according to the invention, used as a part of a continuously operating analyser, is based on the constant volume sampling known as such, the said system also allowing, however, the treatment of the sample for analysis. The sampling and treatment system of the invention takes 30 from a process of a production plant a liquid sample with a predetermined volume, and carries out the treatment, such as the agitation and the precipitation of the sample taken.

According to a preferable embodiment of the invention a precipitating solvent is continuously added to a closed liquid circuit, and accordingly, a respective amount of liquid is removed from this closed circuit, this liquid flowing to the detector that detects the precipitation as the sudden increase (the turning point) of the intensity of 5 the scattered (reflected) light. The parameter (p value, stability) illustrating the tendency to precipitate is calculated from the quantities of the solvents and oil products.

An oil sample with a constant volume is necessary for the calculation of the parameter 10 illustrating the tendency to precipitate, determined by the relative amounts of the oil, the precipitating solvent (a straight-chain hydrocarbon, such as a heptane, pentane, cetane, octane, etc.), and possibly a solvent (xylene, toluene, or another aromatic compound).

15 The sampling and treatment system of the invention is advantageous for the analysis of liquids that are difficult to pump. In addition to homogeneous liquids, the liquid sample may also be a so-called inhomogeneous sol with a high viscosity, or a liquid containing solid particles (a slurry), the invention being, however, applicable to any liquid sample.

20 In the system according to the present invention the mixing during the treatment of the sample is almost ideal, accomplished for instance with a (gear) pump. In the precipitation step, the treatment of the liquid is characterized by the continuous feeding of the precipitating agent (such as heptane) into the mixing loop with a 25 constant volume, as well as by the flow of the liquid volume being displaced through the detector (i.e. the detection of the degree of precipitation). The mixing loop may be equipped with elements that make the mixing more efficient, for instance with a (gear) pump, static mixers, packings, beads etc.

30 The equation for the degree of precipitation is:

$$Q_t = Q_0 \left(1 - e^{-t F_h / V_0}\right)$$

where

- 5 Q_t = concentration of the precipitating agent (e.g. heptane)
- Q_0 = final concentration
- t = time
- V_0 = volume of the sample loop
- F_h = flow of the precipitating agent (e.g. heptane)

10

The above equation may for instance be used for the precise determination of the concentration of the liquid in the sample loop when the concentration measured by the detector is known.

- 15 The automatic sampling and treatment system of the present invention is accompanied with several significant advantages. The sampling, and the treatment of the sample are accomplished in a closed space which is particularly important when handling inflammable or toxic substances. The treated liquid is automatically removed from the sample loop, and recycled to the process during the next sampling
- 20 step, thus reducing the amount of waste and the need to wash the loop. The sampling, and the treatment of the sample are not influenced by the pressure of the process, or pressure variations therein. The sampling, and the treatment of the sample may be automatized easily. The flow to the analyser may be precisely adjusted within a wide range. The reagent used is consumed only in amounts
- 25 necessary for the treatment.

The sampling and treatment system of the present invention is especially suitable for the automatic sampling from the process flow of heavy fuel oil, for an on-line analyser. The sampling and treatment system of the present invention may of course 30 be used for the sampling of any liquid from any process flow.

The invention is now illustrated with reference to the figure of the appended drawing, showing the principle of the invention, naturally without intending to limit the invention exclusively thereto.

- 5 The figure of the drawing shows a preferable embodiment of the sampling and treatment system of the invention as a schematic flow chart.

In the figure of the drawing, the automatic sampling and treatment system of the invention is generally referred to with the numeral 10. The liquid being processed 10 flows in the direction of the arrow A in the process 11. The automatic sampling and treatment system 10 is connected with a first conduit 14, and with a second conduit 16 to the process 11. The conduit 14 is adapted with a valve 13a, and the conduit 16 is adapted with a valve 13b. Preferably, the valves 13a, 13b form a pair of two-way valves that are actuated coincidently. An actuator 12 is adapted to control the valves 15 13a, 13b. Further, the sampling and treatment system 10 comprises a sampling loop 15. The sample stream flows in the direction of the arrow B from the process 11 through the conduit 14 into the sampling loop 15. The sampling loop 15 is preferably equipped with a pump 17. In the sampling loop 15 the sample flows in the direction of the arrow D. In the next samplig step, the treated liquid is automatically 20 removed from the sampling loop 15 through the conduit 16 as the stream C back into the process 11.

The sample stream leaves the sampling loop 15 through a conduit 18 as the stream E towards the analyser. An additive is fed through a conduit 19 into the sampling 25 loop 15. In this embodiment, the additive is fed with a pump 20. The conduit 18 comprises a valve 22a, and the conduit 19 comprises a valve 22b. An actuator 21 is adapted to control the valves 22a, 22b. Preferably the valves 22a, 22b form a pair of two-way valves that are actuated coincidently. The additive flow through the conduit 19 is illustrated with the arrow F.

30

Preferably, in the embodiment shown in this figure the process 11 comprises a flow resistance, in this case a throttling baffle 23. The conduit 18 leading to the analyser

comprises a pressure reducer 24 to prevent excessive liquid from leaking from the sampling loop 15, thus assuring the reliable performance of the sampling and treatment system of the invention. The conduit 19 to convey the additive comprises a return valve 25.

5

The operation of the automatic sampling and treatment system 10 according to the invention is as follows. During sampling, the actuator 12 first opens the sampling loop 15, the liquid from the process stream desired thus displacing the liquid already present in the sampling loop 15. This is facilitated by a pressure difference caused 10 by restricting the flow in the process 11 with a flow resistance, e.g. with a throttling baffle 23, or a separate pump in the sample line (not shown). Also the pump 17 assists in filling the sample loop 15.

At the beginning of the sample treatment, the actuator 12 closes the valves 13a, 13b, 15 that is, it closes the connection between the sampling loop 15, and the process 11. Then, the actuator 21 opens the valves 22a, 22b, thus allowing the additive to flow into the sample loop 15 through the conduit 19. During the sampling and the sample treatment, the sample is effectively circulated by the pump 17 in the sampling loop 15. The additive is fed by the pump 20 into the sampling loop 15 where the mixing 20 is almost ideal. The additive feed displaces a respective amount of liquid that now flows towards the analyser through the conduit 18. The feeding of this precipitating additive is continued until the parameter characterizing the tendency to precipitate is reached. Thereafter, the actuator 21 closes the valves 22a, 22b, and the actuator 12 opens the valves 13a, 13b to allow the sampling loop 15 to receive a new sample. 25 The treated liquid in the sampling loop 15 is automatically removed through the conduit 16 and recycled to the process during the next sampling step, thus reducing the amount of waste being formed and the need to rinse the loop. The flow to the analyser may be precisely adjusted within a wide range with the aid of the pump 20. The reagent fed with the pump 20 is consumed only in amounts necessary for the 30 treatment.

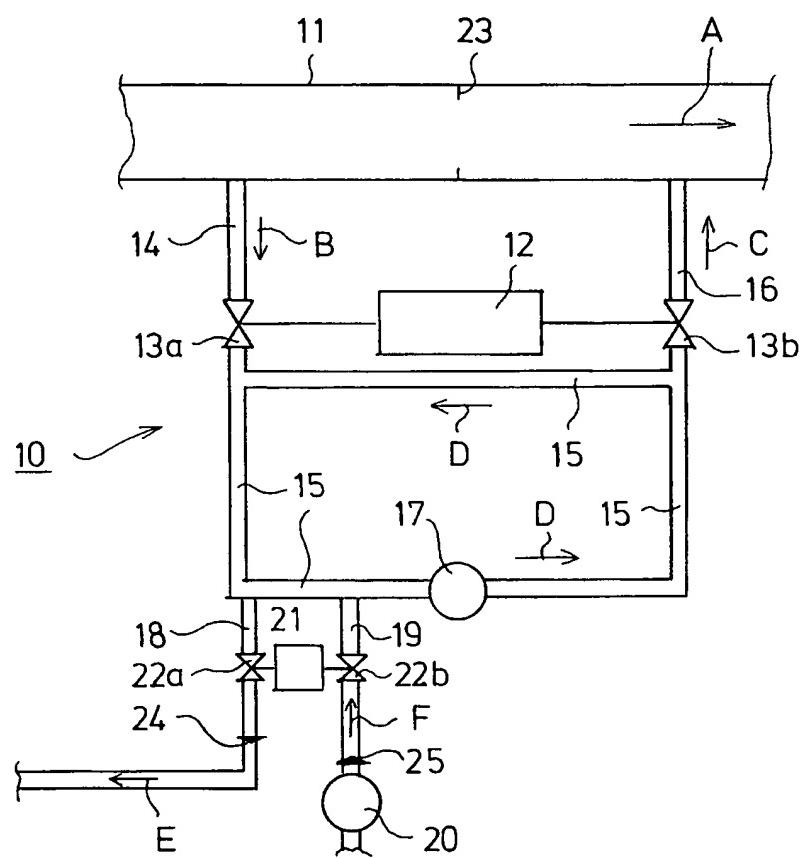
Only the principle of the present invention is presented above, and it is evident to the person skilled in the art that several modifications are possible within the spirit and scope of the invention defined in the appended claims.

Claims

1. Automatic sampling and treatment system (10), comprising a sampling loop (15) connected on-line to a process (11) to receive a sample stream from a stream (A) being processed in the process (11), and further connected to an analyser to convey the sample stream from the sampling loop (15) to the analyser, characterized in that the sampling loop (15) is connected on-line to the process (11) with a first conduit (14), and with a second conduit (16), the sampling loop (15) is connected to an analyser with a third conduit (18), and to a feeding system of an additive with a fourth conduit (19), and that a first actuator (12) is adapted to open and close a valve (13a) in the first conduit (14), and a valve (13b) in the second conduit (16).
5
2. The automatic sampling and treatment system according to the claim 1, characterized in that a second actuator (21) is adapted to open and close a valve (22a) in a third conduit (18), and a valve (22b) in a fourth conduit (19).
10
3. The automatic sampling and treatment system according to the claim 1, characterized in that the valve in the third conduit is a return valve.
15
4. The automatic sampling and treatment system according to any of the above claims 1—3, characterized in that a pump (20) is adapted to feed an additive through the fourth conduit (19) into the sampling loop (15).
20
5. The automatic sampling and treatment system according to the claim 4, characterized in that the additive comprises a precipitating additive.
25
6. The automatic sampling and treatment system according to the claim 5, characterized in that the precipitating additive comprises a straight-chain hydrocarbon, preferably a heptane, pentane, cetane, or octane.
30
7. The automatic sampling and treatment system according to any of the above claims 1—6, characterized in that the sampling loop (15) is equipped with a pump

- (17) adapted to circulate the sample stream, and to support thorough mixing during the sampling, and the sample treatment.
8. The automatic sampling and treatment system according to any of the above
5 claims 1—7, **characterized** in that the treated sample stream is adapted to leave the sampling loop (15) through the second conduit (16) towards the process (11) during the next sampling step.
9. The automatic sampling and treatment system according to any of the above
10 claims 1—8, **characterized** in that the process (11) comprises a flow resistance.
10. The automatic sampling and treatment system according to the claim 9, **charac-**
terized in that the flow resistance is a throttling baffle (23).
- 15 11. The automatic sampling and treatment system according to any of the above claims 1—10, **characterized** in that the third conduit (18) leading to the analyser is equipped with a pressure reducer (24).
12. The automatic sampling and treatment system according to any of the above
20 claims 1—11, **characterized** in that the conduit (19) for feeding the additive is equipped with a return valve (25).
13. The automatic sampling and treatment system according to any of the above
25 claims 1—12, **characterized** in that the valves (13a,13b) in the first and second conduits (14,16), as well as the valves (22a, 22b) in the third and fourth conduits (18, 19) are respectively two-way valves.

1/1



INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 98/00519

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: G01N 1/10, G01N 1/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 9114932 A1 (MüTEK GMBH), 3 October 1991 (03.10.91), page 4, line 28 - page 6, line 20	1,5
Y	---	1
Y	GB 2170909 A (SPECTRA-TEK UK LIMITED), 13 August 1986 (13.08.86), page 1, line 54 - page 2, line 9; page 2, line 52 - line 63	1
A	GB 2206408 A (NIGEL DAVID EVANS), 5 January 1989 (05.01.89), page 4, line 12 - line 24	1-13

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier document but published on or after the international filing date	"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
5 October 1998	07-10-1998
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Ulla Granlund Telephone No. +46 8 782 25 00

Form PCT/ISA/210 (second sheet) (July 1992)

BEST AVAILABLE COPY

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 98/00519

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5275786 A (DONALD D. SOLETA ET AL), 4 January 1994 (04.01.94), column 3, line 30 - line 68 --	1-13
A	GB 2164021 A (JISKOOT AUTOCONTROL LIMITED), 12 March 1986 (12.03.86), page 1, line 32 - line 55 -- -----	1-13

INTERNATIONAL SEARCH REPORT
Information on patent family members

27/07/98

International application No.

PCT/FI 98/00519

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO 9114932 A1	03/10/91	FI 911328 A		21/09/91
		FI 911329 A		21/09/91
GB 2170909 A	13/08/86	NONE		
GB 2206408 A	05/01/89	NONE		
US 5275786 A	04/01/94	US 5213982 A		25/05/93
GB 2164021 A	12/03/86	NONE		